

**ULTRAVIOLET RAYS AND INFRARED RAYS ABSORBING GREEN GLASS**

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**Abstract of JP9208254**

**PROBLEM TO BE SOLVED:** To obtain green glass suppressing the occurrence of defects such as irregularity in color, e.g. a yellow matrix, ream and distortion and having high quality and higher performance by the conventional float process with enhanced productivity in a high yield. **SOLUTION:** This green glass consists essentially of, by weight, 67-75% SiO<sub>2</sub>, 0.05-3.0% Al<sub>2</sub>O<sub>3</sub>, 7.0-11.0% CaO, 2.0-4.2% MgO, 12.0-16.0% Na<sub>2</sub>O, 0.5-3.0% K<sub>2</sub>O, 0.05-0.30% SO<sub>3</sub>, 0.40-0.90% Fe<sub>2</sub>O<sub>3</sub>, 1.0-2.5% CeO<sub>2</sub>, 0.1-1.0% TiO<sub>2</sub>, 0.0010-0.0400% MnO, 0.0001-0.0009% CoO, 0.0001-0.0010% Cr<sub>2</sub>O<sub>3</sub> and 0-1% SnO<sub>2</sub>. The total amt. of these oxides is >=98%, the total amt. of SiO<sub>2</sub> Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> is 70-78%, that of CaO and MgO is 10-15% and that of Na<sub>2</sub>O and K<sub>2</sub>O is 13-17%.

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ULTRAVIOLET AND INFRARED RADIATION ABSORBING GREEN  
GLASS

## [Claims]

[Claim 1] An ultraviolet and infrared radiation absorbing green glass,  
wherein

the glass consists essentially of the below oxides, in weight %:  $\text{SiO}_2$  67 to 75%;  $\text{Al}_2\text{O}_3$  0.05 to 3.0%;  $\text{CaO}$  7.0 to 11.0%;  $\text{MgO}$  2.0 to 4.2%;  $\text{Na}_2\text{O}$  12.0 to 16.0%;  $\text{K}_2\text{O}$  0.5 to 3.0%;  $\text{SO}_3$  0.05 to 0.30%;  $\text{Fe}_2\text{O}_3$  0.40 to 0.90%;  $\text{CeO}_2$  1.0 to 2.5%;  $\text{TiO}_2$  0.1 to 1.0%;  $\text{MnO}$  0.0010 to 0.0400%;  $\text{CoO}$  0.0001 to 0.0009%;  $\text{Cr}_2\text{O}_3$  0.0001 to 0.0010%; and  $\text{SnO}_2$  0 to 1%;

the sum of these components is 98% or more;

the contents of  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2$  are 70 to 76%;

the contents of  $\text{CaO} + \text{MgO}$  are 10 to 15%; and

the contents of  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  are 13 to 17%.

[Claim 2] The ultraviolet and infrared radiation absorbing green glass according to claim 1, wherein the content of  $\text{SnO}_2$  is, in weight %, 0.01 to 0.6%.

[Claim 3] The ultraviolet and infrared radiation absorbing green glass according to claim 1 or 2, wherein when the glass is 5 mm in thickness, a visible light transmittance is 65% or more, a solar radiation transmittance is 30 to 40%, and an ultraviolet ray transmittance is 10% or less, measured with illuminant A; and a dominant wavelength is 500 to 540 nm, and an excitation purity is 5% or less, measured with illuminant  $D_{65}$ .

[0037] It should be noted that the ultraviolet and infrared radiation absorbing green glass of the present invention contains a glass composition capable to be tempered readily. The glass ranges from a thin flat glass of about 1 mm in plate thickness to a thick flat glass of about 15 mm in plate thickness. Examples include a glass with increased hardness that is produced from an untreated glass sheet, a half-tempered glass, a tempered glass or the like, as a flat plate glass or a curved plate glass. These glasses can be used as a single plate glass, a laminated glass, an insulating glass or the like for an architectural window material and, in particular, for an automotive windowpane.

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**[0042] Example 1**

Various glass raw materials were appropriately used. For example, silica sand, feldspar, soda ash, dolomite, limestone, mirabilite, colcothar, titanium oxide, cerium carbonate, ilmenite, carbon, slag, frit glass and cullet.

Examples of the frit glass and the cullet include a clear cullet (C cullet) that contains, in weight %, about 0.09% of  $\text{Fe}_2\text{O}_3$  and about 0.04% of  $\text{TiO}_2$ , a frit glass (NM frit) or a cullet (NM cullet) that mainly contain about 0.675% of  $\text{Fe}_2\text{O}_3$ , about 0.20% of  $\text{TiO}_2$ , about 0.60% of  $\text{CeO}_2$ , or the like. Further examples include a frit glass (H frit) that contains about 0.0960% of  $\text{CoO}$ , a cullet (H cullet) that contains, in weight %, about 0.36% of  $\text{Fe}_2\text{O}_3$  and about 0.0017% of  $\text{CoO}$ . In addition, the glass raw materials include chemical reagents or the like such as  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{NaCO}_3$ ,  $\text{CeO}_2$ ,  $\text{TiO}_2$ , and  $\text{CoO}$ . These components were weighed and combined so that the desired glass composition was obtained as a target composition, and in particular, the rate of reduction that is slightly higher than that of the generally used real furnace (for example, about  $35.5 \pm 5\%$ ) was obtained.

[0043] It should be noted that in the raw material batch, about 1% (about 0.5 to 2%) of mirabilite/(silica sand + feldspar) and about 50% of the cullet were contained, and  $(\text{carbon/hyalinizing amount}) \times 100 = \text{about } 0.16$  was satisfied.

[0044] The prepared raw material was placed in a melting pot, and melted in a real furnace (for example, a lateral side wall portion of an injection port, a side wall portion of a condition portion) that was kept at about  $1450^\circ\text{C}$ , or in an electric furnace of which condition was equal to that of the real furnace, for about 3 to 4 hours so that the material vitrified. Subsequently, in order to homogenize and clarify the glass, the glass was kept at  $1420$  to  $1430^\circ\text{C}$  for about 1.5 to 2 hours, and then, charged into a mold so that a glass block was formed. The resultant glass block was cut into glass plates of about  $100 \text{ mm} \times 100 \text{ mm}$  in size and about 5 mm in thickness and then ground and polished, or the resultant molten glass was cast into a plate shape, whereby each sample was obtained.

[0045] Regarding these samples, the composition of the glass component (weight %) was determined by a wet analytical method or the like based on JIS R-3101. As optical properties (at a thickness of 5 mm), a visible light (wavelength of 380 to 780 nm) transmittance (measured with illuminant A: %), an ultraviolet ray (wavelength of 297.5 to 377.5 nm) transmittance

(measured with illuminant A: %), a solar radiation (wavelength of 340 to 1800 nm) transmittance (measured with illuminant A: %), a dominant wavelength (measured with illuminant D<sub>65</sub>, nm), an excitation purity (measured with illuminant D<sub>65</sub>: %) were examined based on JIS Z-8722, JIS R-3106, and ISO/DIS-9050 with a 340-type UV-Visible Spectrophotometer (manufactured by Hitachi, Ltd.) so that each value was calculated.

[0046] As a result, the composition of the glass component was, in weight %, SiO<sub>2</sub> 69.93%; Al<sub>2</sub>O<sub>3</sub> 1.96%; CaO 7.93%; MgO 3.46%; Na<sub>2</sub>O 12.79%; K<sub>2</sub>O 1.07%; and SO<sub>3</sub> 0.18%. The other components were: Fe<sub>2</sub>O<sub>3</sub> 0.631%; TiO<sub>2</sub> 0.30%; CeO<sub>2</sub> 1.70%; MnO 280 ppm; CoO 2.4 ppm; and Cr<sub>2</sub>O<sub>3</sub> 2.0 ppm, as shown in Table 1. The sum of the components was about 99.979%, and the contents of SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>+TiO<sub>2</sub> was 72.19%, the contents of CaO+MgO was 11.39%, and the contents of Na<sub>2</sub>O+K<sub>2</sub>O was 13.86%. The rate of reduction  $[(\text{FeO}/\text{total Fe}_2\text{O}_3) \times 100]$  was about 35.5%.

[0047] Furthermore, regarding the optical properties, the visible light transmittance was about 67.1%, the solar radiation transmittance was about 37.3%, the dominant wavelength was about 517 nm, the ultraviolet ray transmittance was about 4.8%, and the excitation purity was about 3.3%, as shown in Table 1. The glass had a green color tone, and therefore, it was the desired ultraviolet and infrared radiation absorbing green glass of a high performance that the present invention aimed to achieve.

[0048] It should be noted that a laminated glass was produced experimentally in which a curved ultraviolet and infrared radiation absorbing green glass, of the present invention, of about 2.5 mm in plate thickness was arranged on the outside, and a curved glass plate coated with a heat ray reflective layer, of about 2 mm in plate thickness was arranged on the inside, between which a PVB intermediate layer is inserted with the coated layer being on the inside. The laminated glass was used for an automotive windowpane. It was found that the laminated glass satisfied a standard, which provided a high performance and a multifunctionability offered by the present invention. This further improved the quality of livability and safety inside and outside of the car.

### Example 3

The glass raw material that was the same as that in the Example 2 was used, weighed and combined. A melting operation was then performed. The

resultant glasses were similarly used as samples.

[0053] The resultant samples were analyzed, measured, and evaluated as in the case of the Example 1. As a result, the composition of the glass component was, in weight %,  $\text{SiO}_2$  70.0%;  $\text{Al}_2\text{O}_3$  1.6%;  $\text{CaO}$  8.96%;  $\text{MgO}$  3.04%;  $\text{Na}_2\text{O}$  12.71%;  $\text{K}_2\text{O}$  0.9%; and  $\text{SO}_3$  0.10%. The other components were:  $\text{Fe}_2\text{O}_3$  0.612%;  $\text{TiO}_2$  0.43%;  $\text{CeO}_2$  1.60%;  $\text{MnO}$  280 ppm;  $\text{CoO}$  4.1 ppm; and  $\text{Cr}_2\text{O}_3$  4 ppm, as shown in Table 1. The sum of the components was about 99.981%, and the contents of  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2$  were 72.03%; the contents of  $\text{CaO} + \text{MgO}$  were 12%; and the contents of  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  were 13.61%. The rate of reduction was about 34.6%.

[0054] Regarding the optical properties, as shown in Table 1, the visible light transmittance was about 65.7%, the solar radiation transmittance was about 35.8%, the dominant wavelength was about 512 nm, the ultraviolet ray transmittance was about 4.8%, and the excitation purity was about 3.5%. The glass had a desired green color tone, and therefore, it was the desired ultraviolet and infrared radiation absorbing green glass of a high performance that the present invention aimed to achieve.

[0055] Regarding the property of being readily tempered, the glass sufficiently satisfied a standard defined in JIS, for example, in R 3211 or R 3212. As in the case of the Example 1, even when the glass was a thin glass plate, it was possible to obtain, with high efficiency and yield, a glass that would satisfy the standard.

[0056] Example 4

The glass raw material that was the same as that in the Example 1 was used, weighed and combined. A melting operation was then performed. The resultant glasses were similarly used as samples.

[0057] The resultant samples were analyzed, measured, and evaluated as in the case of the Example 1. As a result, the composition of the basic glass component was the same as that of the Example 1, and had only the coloring components. The other components were:  $\text{Fe}_2\text{O}_3$  0.771%;  $\text{TiO}_2$  0.3%;  $\text{CeO}_2$  1.55%;  $\text{MnO}$  285 ppm;  $\text{CoO}$  4.0 ppm; and  $\text{Cr}_2\text{O}_3$  1ppm, as shown in Table 1. The sum of the components was about 99.970%, and the contents of  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2$  were 72.19%; the contents of  $\text{CaO} + \text{MgO}$  were 11.39%; and the contents of  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  were 13.86%. The rate of reduction was about 27.5%.

[0058] Regarding the optical properties, as shown in Table 1, the visible light



transmittance was about 65.5%, the solar radiation transmittance was about 34.5%, the dominant wavelength was about 519 nm, the ultraviolet ray transmittance was about 4.5%, and the excitation purity was about 3.8%. The glass had a desired green color tone, and therefore, it was the desired ultraviolet and infrared radiation absorbing green glass of a high performance that the present invention aimed to achieve.

[0059] Example 5

The glass raw material that was the same as that in the Example 2 was used, weighed and combined. A melting operation was then performed. The resultant glasses were similarly used as samples.

[0060] The resultant samples were analyzed, measured, and evaluated as in the case of the Example 1. As a result, the composition of the basic glass component was the same as that of the Example 2, and had only the coloring components. The other components were:  $\text{Fe}_2\text{O}_3$  0.635%;  $\text{TiO}_2$  0.44%;  $\text{CeO}_2$  1.61%;  $\text{MnO}$  280 ppm;  $\text{CoO}$  4.0 ppm; and  $\text{Cr}_2\text{O}_3$  5 ppm, as shown in Table 1. The sum of the components was about 99.674%, and the contents of  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2$  were 71.74%; the contents of  $\text{CaO} + \text{MgO}$  were 12%; and the contents of  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  were 13.54%. The rate of reduction was about 38.2%.

[0061] Regarding the optical properties, as shown in Table 1, the visible light transmittance was about 66.4%, the solar radiation transmittance was about 33.1%, the dominant wavelength was about 507 nm, the ultraviolet ray transmittance was about 5.0%, and the excitation purity was about 4.3%. The glass had a desired green color tone, and therefore, it was the desired ultraviolet and infrared radiation absorbing green glass of a high performance that the present invention aimed to achieve.

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[Table 1]

	Example 1	Example 3	Example 4	Example 5
Fe <sub>2</sub> O <sub>3</sub> (wt.%)	0.631	0.612	0.771	0.635
FeO (wt.%)	0.224	0.212	0.212	0.243
CeO <sub>2</sub> (wt.%)	1.70	1.60	1.55	1.61
TiO <sub>2</sub> (wt.%)	0.30	0.43	0.30	0.44
MnO (ppm)	280	280	285	280
CoO (ppm)	2.4	4.1	4.0	4.0
Cr <sub>2</sub> O <sub>3</sub> (ppm)	2.0	4.0	1.0	5.0
FeO/ $\Sigma$ Fe <sub>2</sub> O <sub>3</sub> (%)	35.5	34.6	27.5	38.2
Visible light transmittance(%)	67.1	65.7	65.5	66.4
Solar radiation transmittance(%)	37.3	35.8	34.5	33.1
Ultraviolet ray transmittance(%)	4.8	4.8	4.5	5.0
Dominant wavelength(%)	517	512	519	507
Excitation purity(%)	3.3	3.5	3.8	4.3
Addition amount of carbon(%)	0.16	0.16	0.205	0.10